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(54) Title: MAGNETIZABLE DEVICE (57) Abstract There is disclosed a magnetic recording medium which includes a magnetizable layer thereon, wherein said magnetizable layer comprises a plurality of ferri- or ferromagnetic particles each having a largest dimension no greater than 100nm, and each of which particles represents a separate ferromagnetic domain.		

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MAGNETIZABLE DEVICE

This invention relates to a magnetizable device which comprises a magnetic layer composed of domain-separated, nanoscale (e.g. 1-100nm) ferromagnetic particles. The magnetizable device of the invention may be used as a magnetic storage device having improved data storage characteristics. In particular, the invention relates to magnetic storage media comprising single-domain, domain-separated, uniform, ferromagnetic nanoscale (e.g. 1-100 nm) particles which may be arranged into a regular 2-D packed array useful in the storage of information.

Among the possible pathways to ultrahigh-density (≥ 1 Gbit/in²) magnetic media is the use of nanoscale (1-100 nm) particles. Beyond the standard requirements for magnetic media, a viable particulate media should have a small standard deviation in particle size as well as the particles being exchange decoupled. These requirements are necessary to avoid adverse media noise. Current methods of fabricating nanoscale particles, such as arc-discharge or multiple target ion-beam sputtering, have not fully addressed these two requirements. Moreover, if the uniform particles are arranged into an ordered array, each particle can represent a "bit" of information at a predictable location further increasing the media's efficiency. This invention details methods of producing particulate media that meet these requirements for ultrahigh-density recording. This invention is also an open system which allows for the production of a variety of magnetic materials, such that the media can be tuned for different applications.

In particular this invention details the use of an iron storage protein, ferritin, whose internal cavity is used to produce the nanoscale particles. Ferritin is utilised in iron metabolism throughout living

species and its structure is highly conserved among them. It consists of 24 subunits which are arranged to provide a hollow shell roughly 8 nm in diameter. The cavity normally stores 4500 iron(III) atoms in the form of paramagnetic ferrihydrite. However, this ferrihydrite can be removed (a ferritin devoid of ferrihydrite is termed "apoferritin") and other materials may be incorporated. Examples include ceramics, superparamagnetic magnetite, acetaminophen, and even the sweetener aspartame. To address magnetic media concerns, the invention incorporates ferromagnetically ordered materials.

According to a first aspect of the present invention, there is provided a magnetizable device which comprises a magnetic layer composed of domain-separated, ferromagnetic particles each of which has a largest dimension no greater than 100nm.

According to a second aspect of the invention, there is provided a magnetic recording medium which includes a magnetizable layer, wherein said magnetizable layer comprises a plurality of ferromagnetic particles each having a largest dimension no greater than 100nm, and each of which particles represents a separate ferromagnetic domain. The magnetizable layer is preferably supported on a non-magnetic substrate.

According to a third aspect of the present invention, there is provided a magnetic composition comprising a plurality of ferromagnetic particles each of which is bound to an organic macromolecule, and each of which has a largest dimension no greater than 100nm. In this aspect of the invention, it is preferred that said organic macromolecule is ferritin from which the normal core ferrihydrite has been removed and replaced by a ferromagnetic particle.

As used herein, the term "ferromagnetic" embraces

materials which are either "ferromagnetic" and "ferrimagnetic". Such usage is common in the electrical engineering art.

The ferromagnetic particles used in the invention
5 should be of a material and size such that they possess ferromagnetic properties at ambient temperatures (e.g. 15°C to 30°C),

Preferably, the ferromagnetic particles each have a largest dimension no greater than 50nm, more
10 preferably less than 25nm and most preferably smaller than 15nm. The largest dimension of the ferromagnetic particles should not be so small that the particle will lose its ferromagnetic property and become
superparamagnetic at the desired operating temperature
15 of the recording medium. Typically, for operation at ambient temperature, this means that the magnetic particles will normally be no smaller than about 3nm in their largest diameter.

In the magnetizable device of the first aspect of
20 this invention and the magnetic recording medium of the second aspect of this invention, the distance between adjacent ferromagnetic domains is preferably as small as possible to permit the maximum number of discrete domains in a given area, and provide the maximum
25 storage capacity for the recording medium. The actual lower limit will vary for different materials and other conditions such as the temperature at which the recording medium is to be used. The key requirement, however, is that neighbouring domains should not be
30 able to interfere magnetically with each other to the extent that the magnetic alignment of any domain can be altered by neighbouring domains. Typically, the lower limit on the spacing of the domains is about 2nm. The distance between adjacent domains will be determined by
35 the density of discrete domains required. Typically, however, to take advantage of the miniaturization

possibilities provided by the invention, the distance between adjacent domains will be no greater than 10nm.

Generally the particles will be uniform in size, by which we mean that the particles do not vary in largest diameter by more than about 5%. One of the advantages of the use in the invention of an organic macromolecule which binds a magnetic particle by surrounding it is that this can be used to select particles of a uniform size.

10 In the case where the particles are spheroidal, it will be the diameter of the particles which must be no greater than 100nm.

In preferred embodiments of all aspects of this invention, each ferromagnetic particle is encased, or partially encased, within an organic macromolecule. The term macromolecule means a molecule, or assembly of molecules, and may have a molecular weight of up to 1500kD, typically less than 500kD. Ferritin has a molecular weight of 400kD.

20 The macromolecule should be capable of binding by encasing or otherwise organising the magnetic particle, and may therefore comprise a suitable cavity capable of containing the particle; a cavity will normally be fully enclosed within the macromolecule.

25 Alternatively, the macromolecule may include a suitable opening which is not fully surrounded, but which nevertheless is capable of receiving and supporting the magnetic particle; for example, the opening may be that defined by an annulus in the macromolecule. For

30 example, suitable macromolecules which may be used in the invention are proteins, for example the protein apoferritin (which is ferritin in which the cavity is empty), flagellar L-P rings, cyclodextrins, self-assembled cyclic peptides. As an alternative to

35 encasing the magnetic particles within the macromolecule, they may be organised on the

macromolecule, such as on a bacterial S-layer.

Other materials which may be used in the invention to organise the ferromagnetic particles are inorganic-silica networks such as MCM type materials, dendrimers and micellar type systems.

The presently preferred macromolecule for use in the invention is the apoferritin protein which has a cavity of the order of 8nm in diameter. The ferri- or ferromagnetic particles to be accommodated within this protein should have a diameter no greater than 8nm.

The bound particles of this aspect of the present invention with a coating that inhibits aggregation and oxidation, also helping them to be domain-separated.

In the magnetizable device of the first aspect of this invention and the magnetic recording medium of the second aspect of this invention, the particles are preferably arranged in a 2-D ordered array which would yield an ultrahigh-density magnetic media.

The ferromagnetic material may be a metal, such as cobalt, iron, or nickel; a metal alloy, such as an alloy which contains aluminium, barium, bismuth, cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, praseodymium, samarium, strontium, titanium, vanadium, ytterbium, yttrium or a mixture thereof; a metal ferrite such as a ferrite containing barium, cobalt, or strontium; or an organic ferromagnetic material.

When generating nanoscale particles, one major concern is that the particles produced are not superparamagnetic. Superparamagnetic particles are those which have permanent magnetic dipole moments, but the moments' orientations with respect to the crystallographic axes fluctuate with time. This is not useful for a practical magnetic storage media. Superparamagnetism depends on the volume, temperature, and anisotropy of the particles. Via energy

considerations, one can derive an equation relating these quantities. The volume at which a particle becomes superparamagnetic (V_p) is given by: $V_p = 25kT/K$, where k is Boltzman's constant, T the temperature of the particle in degrees Kelvin, and K the anisotropy constant of the material. Using this formula, it is possible to determine the temperature at which a particle becomes superparamagnetic (the "blocking temperature") for a given material at a fixed volume. In our specific case, the fixed volume is 8 nm in ferritin. If a cobalt metal particle with only crystalline anisotropy (that value being 45×10^5) is a sphere with a diameter of 8 nm, the blocking temperature is 353 °K. This is within the range of temperatures experienced within a hard disk drive, and the cobalt particles may prove to be a useful storage medium. Obviously, there are other considerations such as the materials' coercivity, moment, saturation magnetisation, and relaxation time. By tuning the materials incorporated into the ferritin, though, these can be addressed.

Ferritin is utilised in iron metabolism throughout living species and its structure is highly conserved among them. It consists of 24 subunits arranged in a 432 symmetry which provide a hollow shell roughly 8 nm in diameter. The cavity normally stores 4500 iron(III) atoms in the form of paramagnetic ferrihydrite. However, this ferrihydrite can be removed (a ferritin devoid of ferrihydrite is termed "apoferritin") and other materials may be incorporated. The subunits in ferritin pack tightly, however there are channels into the cavity at the 3-fold and 4-fold axes. Lining the 3-fold channels are residues which bind metals such as cadmium, zinc, and calcium. By introducing such divalent ions one can potentially bind ferritin molecules together, or at least encourage their

proximal arrangement.

One method of preparing a 2-D packed array of ferromagnetically ordered particles of uniform size up to 8 nm includes the removal of the ferrihydrite core from the native ferritin in aqueous solution, the
5 incorporation of ferromagnetically ordered cobalt metal particles by sodium borohydride reduction of the aqueous Co(II) solution into the ferritin cavities, the generation of a narrow size distribution through
10 ultracentrifugation, the injection of particles into an MES/glucose subphase solution upon which the 2-D array assembles, and the transfer of the 2-D array to a substrate which is then carbon coated. In this method, the ferritin source may be a vertebrate, invertebrate,
15 plant, fungi, yeast, bacteria, or one produced through recombinant techniques.

In the method described, a metal alloy core may be produced by sodium borohydride reduction of a water soluble metal salt. Other oxidation methods include
20 carbon, carbon monoxide, hydrogen, or hydrazine hydrate solution. Alternatively, a suitable solution may be oxidised to yield a metal ferrite core. Oxidation may be chemical or electrochemical to yield the metal ferrite.

25 In this method, other methods of selecting a narrow size distribution may be employed such as short or long column meniscus depletion methods or magnetic field separation.

Further, in this method, divalent metal salts
30 containing cadmium, calcium, or zinc may be added into the subphase solution to aid in particle ordering.

Further, in this, other methods of arranging the particles into a 2-D array may be employed, such as solution evaporation onto a solid substrate.

35 Further, in this method, the 2-D array may be coated with carbon-based films such as hydrogenated or

nitrogen doped diamond-like carbon, or with silicon-based films such as silicon dioxide.

In the present invention, ferritin may be used to enclose a ferromagnetic particle whose largest dimension is limited by ferritin's inner diameter of 8 nm. The particles are produced first by removing the ferrihydrite core to yield apoferritin. This is done by dialysis against a buffered sodium acetate solution under a nitrogen flow. Reductive chelation using thioglycolic acid is used to remove the ferrihydrite core. This is followed by repeated dialysis against a sodium chloride solution to completely remove the reduced ferrihydrite core from solution. Once the apoferritin is produced, ferri- or ferromagnetic particles are incorporated in the following ways. The first is by reducing a metal salt solution in the presence of apoferritin. This is performed in an inert atmosphere to protect the metal particles from oxidation which would lessen their magnetic benefit. A combination of metal salts in solution can also be reduced to generate alloys or alloy precursors. Sintering or annealing in a magnetic field may be necessary to generate the useful magnetic alloys. Another method is to oxidise a combination of an iron(II) salt and another metal salt. This gives a metal ferrite particle which does not suffer negatively from oxidation. The metal salts which are beneficial include salts of aluminium, barium, bismuth, cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, praseodymium, samarium, strontium, titanium, vanadium, ytterbium, and yttrium.

A narrow size distribution of particles is necessary to avoid media noise. Such a distribution can be obtained through a variety of procedures including, but not limited to, density gradient

centrifugation or magnetic field separation.

While the production procedure detailed uses native horse spleen ferritin, this invention should not be seen as limited to that source. Ferritin can be found in vertebrates, invertebrates, plants, fungi, yeasts, bacteria, or even produced through recombinant techniques. By creating mutant apoferritins lacking the divalent binding site, others have found that the mutant proteins assemble into oblique assemblies as opposed to the regular hexagonal close-packed.

While ferritin seems to be an ideal system for generating nanoscale particles, it is not the only system available. For example, flagellar L-P rings are tubular proteins with an inner diameter of 13 nm. By creating a 2-D array of these proteins, metal films could be deposited into the tubular centres to create perpendicular rods of magnetic material. Also metal reduction in the presence of a microemulsion can be used to generate nanoscale particles which are coated with surfactant. This invention is open to other nanoscale particle production methods.

Finally an ordered arrangement of the particles is desired. One way to accomplish this is by injecting an aqueous solution of particles into an MES/glucose subphase solution contained in a Teflon trough. The particles spread at the air-subphase interface, and a portion denature to form a monolayer film. The 2-D arrangement of encased particles occurs underneath this monolayer. After 10 minutes at room temperature, the arrangement and monolayer are transferred to a substrate by placing the substrate directly onto the monolayer for 5 minutes. After withdrawing the substrate, the attached arrangement is coated with a thin layer of carbon for protection. Other methods such as solution evaporation onto a solid substrate can also give 2-D arrangements, and this invention should

not be seen as limited in its arrangement methods.

EXAMPLE 1

This example illustrates the preparation of apoferritin from horse spleen ferritin. Apoferritin
5 was prepared from cadmium-free native horse spleen ferritin (CalBiochem, 100 mg/ml) by dialysis (molecular weight cut-off of 10-14 kDaltons) against sodium acetate solution (0.2 M) buffered at pH 5.5 under a nitrogen flow with reductive chelation using
10 thioglycolic acid (0.3 M) to remove the ferrihydrite core. This is followed by repeated dialysis against sodium chloride solution (0.15 M) to completely remove the reduced ferrihydrite core from solution.

EXAMPLE 2

15 This example illustrates the preparation of cobalt metal within apoferritin. The apoprotein is added to a deaerated TES/sodium chloride solution (0.1/0.4 M) buffered at pH 7.5 to give an approximate 1 mg/ml working solution of the protein. A deaerated
20 cobalt(II) [for example, as the acetate salt] solution (1 mg/ml) was added incrementally such that the total number of atoms added was approximately 500 atoms/apoprotein molecule. This was allowed to stir at room temperature for one day in an inert atmosphere.
25 This is followed by reduction of the cobalt(II) salt with sodium borohydride to cobalt(0) metal. The final product yielded a solution of cobalt particles, each surrounded by a ferritin shell.

EXAMPLE 3

30 This example illustrates the preparation of a metal alloy such as yttrium cobalt (YCo_5) within apoferritin. The metal alloy follows the same procedure as Example 2 but using a 1:5 ratio of yttrium(III) [for example, as the acetate salt] to cobalt(II) [for
35 example, as the acetate salt]. The final product yielded a solution of yttrium cobalt particles, each

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surrounded by a ferritin shell.

EXAMPLE 4

This example illustrates the preparation of a metal ferrite such as cobalt ferrite ($\text{CoO} \cdot \text{Fe}_2\text{O}_3$) within apoferritin. The apoprotein is added to a deaerated MES/sodium chloride solution (0.1/0.4 M) buffered at pH 6 to give an approximate 1 mg/ml working solution of the protein. A deaerated solution of cobalt(II) [for example, as the acetate salt] and iron(II) [for example, as the ammonium sulphate salt] in a ratio of 1:2 is added incrementally and allowed to air-oxidise. The final product yielded a solution of cobalt ferrite particles, each surrounded by a ferritin shell.

EXAMPLE 5

This example illustrates the 2-D arrangement of ferritin-encased magnetic particles. An aqueous solution of particles [from Examples 2-4, and whose uniformity in size has been selected] is injected into an MES/glucose subphase solution (0.01 M/2%) contained in a Teflon trough. The particles spread at the air-subphase interface, and a portion denature to form a monolayer film. The 2-D arrangement of encased particles occurs underneath this monolayer. After 10 minutes at room temperature, the arrangement and monolayer are transferred to a substrate by placing the substrate directly onto the monolayer for 5 minutes. After withdrawing the substrate, the attached arrangement is coated with a thin layer of carbon for protection.

CLAIMS:

1. A magnetizable device which comprises a magnetic layer composed of domain-separated, ferromagnetic particles each of which has a largest
5 dimension no greater than 100nm.

2. Magnetic recording medium which includes a magnetizable layer thereon, wherein said magnetizable layer comprises a plurality of ferromagnetic particles each having a largest dimension no greater than 100nm,
10 and each of which particles represents a separate ferromagnetic domain.

3. Magnetic recording medium according to claim 2, wherein the distance between adjacent ferromagnetic domains is at least 2nm.

15 4. Magnetic recording medium according to claim 2 or 3, wherein the distance between adjacent ferromagnetic domains is no greater than 10nm.

5. Magnetic recording medium according to claim 1, 2, 3 or 4, wherein each ferromagnetic particle is
20 encased within an organic macromolecule.

6. Magnetic recording medium according to claim 5, wherein each ferromagnetic particle is encased within the cavity or opening of a protein macromolecule.

25 7. Magnetic recording medium according to claim 6, wherein each ferri- or ferromagnetic particle is encased within an apoferritin protein.

8. A magnetic composition comprising a plurality of ferromagnetic particles each of which is bound to an
30 organic macromolecule, and each of which ferromagnetic particles has a largest dimension no greater than 100nm.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G11B5/712 G11B5/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 574 961 A (EDELSTEIN ALAN S ET AL) 12 November 1996	1,2
A	see column 3, line 51 - line 60 see column 4, line 58 - line 64 see column 7, line 29 - line 46 see column 8, line 39 - line 55	3
X	EP 0 586 052 A (XEROX CORP) 9 March 1994	8
A	see column 16, line 56 - column 17, line 7 see claims 1-4 see column 17	1-7
A	HONG J ET AL: "GRANULAR MAGNETIC COBALT METAL/POLYMER THIN FILM SYSTEM" IEEE TRANSACTIONS ON MAGNETICS, vol. 32, no. 5, September 1996, pages 4475-4477, XP000634042 see abstract	1-8
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 491 219 A (MANN STEPHEN) 13 February 1996 see claims 1-11	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/03152

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5574961 A	12-11-96	NONE	
EP 0586052 A	09-03-94	US 5358659 A	25-10-94
		DE 69310459 D	12-06-97
		DE 69310459 T	27-11-97
		JP 2648557 B	03-09-97
		JP 6077037 A	18-03-94
		US 5567564 A	22-10-96
		US 5670078 A	23-09-97
US 5491219 A	13-02-96	NONE	